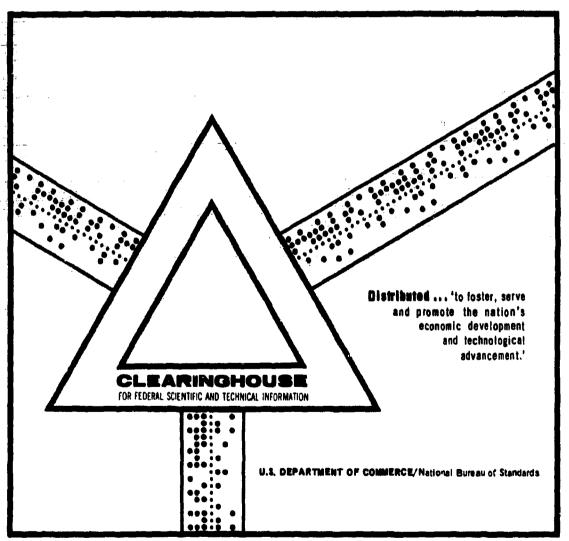
CONSEQUENCES OF ENVIRONMENTALLY INDUCED DILATATION IN SOLIDS

J. C. Halpin, et al

Air Force Materials Laboratory Wright-Patterson Air Force Base, Ohio

December 1969



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J. C. HALPIN and N. J. PAGANO

TECHNICAL REPORT AFML-TR-68-395

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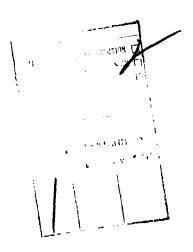
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J. C. HALPIN and N. J. PAGANO

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FOREWORD

This report was prepared by J. C. Halpin of the Elastomers and Coatings Branch, and N. J. Pagano of the Plastics and Composites Branch, Nonmetallic Materials Division, Air Force Materials Laboratory. The work was conducted under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena," Task No. 734202, "Studies on the Structure-Property Relationships of Polymeric Materials," and was administered by the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio.

Research reported occurred December 1967 to August 1968. The report was released by the authors in June 1969 for publication.

This technical report has been reviewed and is approved

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ABSTRACT

The deformation of a solid induced by swelling is equivalent to that caused by a temperature change. A generalized Duhamel-Neumann form of Hooke's law is employed to treat a wide variety of environmental problems by the joint application of solid mechanics and elementary physical chemistry. This approach is illustrated for a swellen fiber reinforced material, employing physical chemistry concepts, micromechanics, and laminated anisotropic plate theory. The specific results are applicable to the design of dimensionally stable composite materials in variable thermal or swelling environments. A new strain invariant for laminates under these types of environments is also introduced.

Distribution of this abstract is unlimited.

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INTRODUCTION

A general phenomenon of nature is the dilatation of a solid induced by a variety of causes. Some reasons for this phenomenon are: an increase in temperature; absorption or loss of swelling agents such as water, organic solvents, etc; and the sudden expansion of absorbed gases in a solid. These natural processes are responsible for such effects as thermal stresses and the swelling stresses (References 1 and 2) to be discussed in this report.

Swelling stresses are often involved in environmental cracking of solids and the internal fracture of a solid after it is subjected to laser radiation focused on internal planes of the material. In the latter illustration, stresses are induced by the combined action of locally large thermal expansions and the rapid expansion of volatile products from the thermal decomposition of the solid. In the everyday world these forces are seen in the cracking of soil as it dries, the expansion of door jambs and window sashes in humid weather, and the cracking of paint as it dries. Figure 1 is a photograph of a rubber block which was swellen and subsequently dried out, primarily by nonuniform evaporation. The resulting stresses fractured the block in a cracking pattern similar to that observed in dried soil or on a painted surface.

Despite the considerable work devoted to thermal expansion and thermal stress problems, the current literature does not provide a general basis for formulating an analysis of such diverse yet related phenomena as outlined above. The importance to modern engineering technology and the biological sciences, however, has prompted this attempt at an analysis of the consequences of such phenomena. For the sake of brevity and laboratory convenience, we shall analyze the phenomenon of swelling as an illustrative example and show how this problem parallels the related thermal problem.

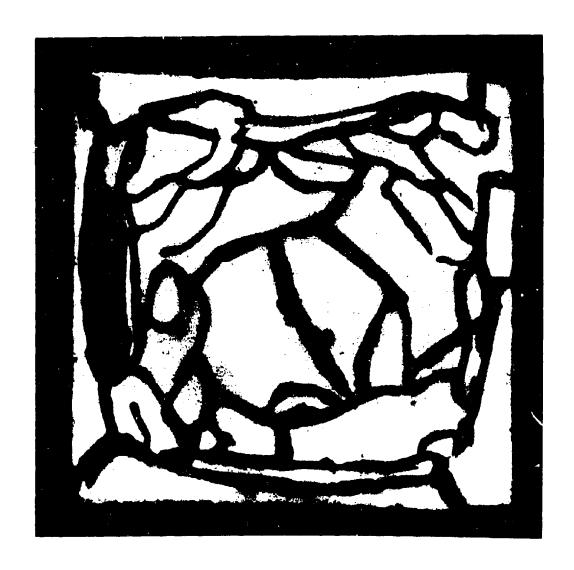


Figure 1. Cracking Pattern Induced in a Solid by Swelling Stresses

EXPANSIONAL STRAINS

In this section we shall establish the procedures for the computation of strain when an object is deformed by swelling or internal gas expansion. With swelling we are concerned with the equilibrium existing between at least two phases. The simplest case to consider is that in which one phase contains two components, while the other contains only one. We shall have a particular interest in the specific case where the mixed phase is solid and the pure phase liquid.

The absorption of a vapor or liquid by a solid is a natural process, not uniquely dependent on any specific attraction between the solid in question and the swelling agent, but rather on the general diffusing tendency of two sets of molecules. This diffusing tendency is no different, in principle, from that existing between two liquids of similar chemical constitution: for example, the mixing of alcohol and water. These remarks are particularly true for organic polymeric materials absorbing organic vapors and fluids, which are predominantly entropy controlled processes. However, for some water-swelling materials, the driving force in the swelling process is the chemical attraction between water and solid, which is effective in spite of an adverse entropy reduction. Detailed discussions on these points are available in standard tests (References 3 - 6) on theory of solutions.

The extent of swelling will be defined by the volume fraction v_2 of solid in the mixture of solid and liquid. On absorbing a quantity of vapor or liquid a unit isotropic cube in the dry state deforms into a cube of edge λ . The volume swelling ratio for an incompressible solid will then be given by $1/v_2$ or λ^3 . The normal strain corresponding to this volume change is defined as

$$\epsilon = \lambda - 1 = (1/v_2)^{1/3} - 1$$
 (1)

for small strains, ϵ . These definitions are independent of the nature of the swelling agent or of the question of equilibrium between the specific fluid and swollen solid. We consider v_2 as a parameter which defines the state of strain in an unstressed swollen infinitesimal volume element. It is sufficient at this

point to simply recognize that procedures exist in the physical chemistry of mixtures and solutions (Reference 3) which allow for the prediction of v_Z for specific combinations of fluids and solids.

During the performance of our conceptual experiment the isotropic body was observed to undergo a pure volume dilatation in the absence of surface tractions. If it were only required that we pass from the initial volume to the final volume under no surface tractions, the same state of hydrostatic strain, ϵ , could have been produced by a simple temperature rise. A thermal expansion is therefore the mechanical equivalent of a swelling process.

We are now in a position to consider the form of the constitutive relations in a more general environmental state. Performing the well known power series expansion of the strain energy function we have

$$2W = C_0 + C'_{ij} e_{ij} + C_{ijkl} e_{ij} e_{kl} + ---$$
 (2)

where the coefficients C_0 , C_{ij} , stc. are functions of the entropy, the temperature, and such composition variables as v_2 . Since W = 0 when $e_{ij} = 0$ by definition, the constant C_0 must vanish. Furthermore, since

$$\sigma_{ij} = \frac{\partial W}{\partial e_{ij}} = \frac{1}{2} C'_{ij} + O(e_{ij})$$
 (3)

 C_{ij}^{i} must be equal to $2\sigma_{ij}^{i}$ at zero strain. Such stresses occur in a solid that is completely constrained against deformations caused by environmental factors such as swelling and change in temperature. In what follows we shall call these deformations expansional strains ϵ_{ij}^{i} . The simplest assumption to treat these effects is to allow C_{ij}^{i} to be proportional to the expansional strains, i.e.,

$$C'_{ii} = -2C_{iikl} \epsilon_{kl} \tag{4}$$

where $\epsilon_{k!} = \alpha_{k!} \Delta T$ for temperature changes and to employ Equation 1 for calculating expansional strains due to swelling or internal gas expansion. When we drop higher than second order terms in the strain energy density, we get

$$W = -C_{ijkl} e_{ij} \epsilon_{kl} + \frac{1}{2}C_{ijkl} e_{ij} e_{kl}$$
 (5)

Hence, the stress components are given by

$$\sigma_{ii} = C_{iikl} \left(\mathbf{e}_{kl} - \boldsymbol{\epsilon}_{kl} \right) \tag{6}$$

which is a more general version of the Duhamel-Neumann form of Hooke's Law. The inverse of Equation 6 is then

$$\mathbf{e}_{ii} = \mathbf{S}_{iikl} \, \sigma_{kl} + \boldsymbol{\epsilon}_{ii} \tag{7}$$

where Siikl is the compliance tensor.

Since the expansional strains are the components of a second order tensor, they must obey the tensor transformation law

$$\epsilon'_{ij} = t_{ki} t_{ij} \epsilon_{kl}$$
 (8)

where t_{ij} are the direction cosines between x_i and x_j . For the specific case of an orthotropic material, where unprimed coordinates refer to the axes of material symmetry, the expansional shear strains are zero and Equation 8 reduces to

$$\epsilon'_{ij} = t_{i1} t_{j1} \epsilon_{j1} + t_{i2} t_{j2} \epsilon_{22} + t_{i3} t_{i3} \epsilon_{33}$$
 (9)

An experimental verification of this transformation law will be given in a subsequent section.

For an isotropic solid, Equation 7 reduces to

$$e_{ij} = \frac{1}{2G} \sigma_{ij} - (\frac{1}{6G} - \frac{1}{9K}) \theta \delta_{ij} + \epsilon \delta_{ij}$$
 (10)

where δ_{ij} is the Kronecker delta, G the shear modulus, K the bulk modulus, $\theta = \sigma_{ij}$, and ϵ is the linear expansional strain defined by Equation 1 for swelling and by $\alpha\Delta T$ for thermal expansion. In the general case, small expansional strains from different sources are additive so that

The corresponding strain energy function is given by

$$W = \frac{1}{4G} \sigma_{ij} \sigma_{ij} - (\frac{1}{12G} - \frac{1}{18K}) \theta^2 - \epsilon \theta$$
 (12)

Accordingly, we may conclude this section by noting that any physical process which yields an expansional strain can be formulated into a boundary value problem within the framework of formal elasticity theory. In fact, solutions obtained in thermal elasticity can be extended to general expansional problems by the substitution of ϵ_{ij} for $\alpha_{ij}\Delta T$. This statement should also be valid not only for uniform expansional fields but also for problems where expansional gradients are of concern. Where the properties of a thermal gradient and thermal diffusion are expressed in Fourier's law (Reference 7), the problem of gas, vapor, or liquid diffusion and concentration gradient will be governed by Fick's law (References 1 and 8).

A problem in expansional elasticity shall be discussed and tested experimentally in the next section. The problem is to establish as a function of constituent material properties the expansional strains in a thin heterogeneous sheet submerged in a swelling liquid and then to predict the swelling properties of an angle-ply laminate constructed of this heterogeneous material.

The problem of an advancing boundary of swollen material within a homogeneous isotropic cylindrical body has been treated by Alfrey, Gurnee, and Lloyd (Reference 1) by use of elasticity theory. Our prime concern in subsequent sections, however, will be to study the influence of swelling in heterogenous anisotropic systems.

ANALYSES OF A UNIDIRECTIONAL COMPOSITE SHEET

The prediction of the elastic and thermal properties of unidirectional composites as functions of constituent material properties and phase geometry has received considerable attention in recent years (References 9 and 10). Very recently Schapery (Reference 11) has derived upper and lower bounds as well as convenient approximate expressions for thermal expansion coefficients based on the principles of minimum potential and complementary energy. We shall now demonstrate that Schapery's solutions are equally valid for expansional strains induced by a swelling agent.

Because our argument is dependent on experimental verification we have chosen, for experimental ease, an elastomeric matrix material reinforced with a system of parallel nylon textile cords for the demonstration. The mechanical characterization and the special experimental techniques required for orthotropic materials has previously been reported in References 12 and 13.

The constituent materials properties are as given below, where the subscript f stands for fiber and m for matrix:

E, = 292,000 psi

E_ = 300 psi

 $\nu_e = 0.2$

ν_ = 0.4999

The composite moduli below were determined experimentally and are in agreement with the micromechanics prediction of Hermans (Reference 14):

E .. = 132,000 psi

E 22 = 1050 psi

ν₁₂ = 0.36

G₁₂ = 263 psi

where E_{11} and E_{22} are the respective Young's moduli parallel and normal to the fiber direction, ν_{12} is Poisson's ratio measuring transverse contraction under a uniaxial stress acting parallel to the fibers, and G_{12} is the shear

modulus with respect to the axes parallel and normal to the fibers. Owing to its high degree of anisotropy, this material offers a stern test for the hypothesis presented above.

We shall first offer a graphical demonstration of the transformation property of ϵ_{ij} , i.e., Equation 9. This was achieved by immersing unidirectional sheets possessing different fiber orientations in an efficient swelling agent for the matrix, namely benzene. Results of a typical experiment are shown in Figure 2(a) for a 30-degree specimen in the dry and swollen states.

In the performance of the experiment the specimens were observed to undergo rather large strains invalidating the assumption of infinitesimal deformations. Accordingly, to obtain a precise comparison of theory and experiment, one must employ a geometrically nonlinear measure of strain. We shall utilize the Lagrangian or Green strain tensor defined (Reference 7) as

$$2e_{jk} * u_{j,k} + u_{k,j} + u_{i,j} u_{i,k}$$
 (13)

with

The extensional strains were computed as

$$\epsilon_{11} = \frac{1}{2} \left[\left(\epsilon_1 + 1 \right)^2 - 1 \right]$$

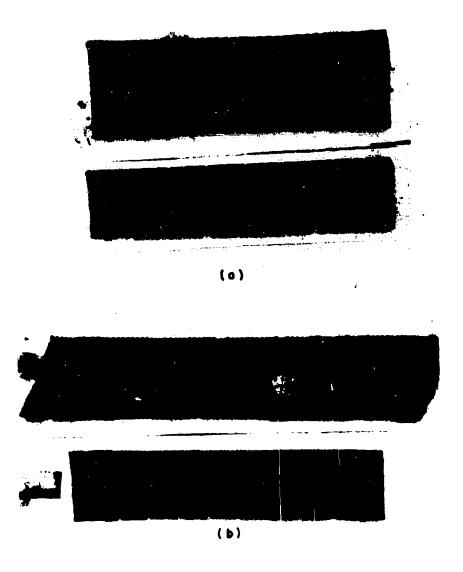
and

$$\epsilon_{22} = \frac{1}{2} \left[\left(E_2 + I \right)^2 - I \right] \tag{14}$$

where $E = \Delta 1/1$. The corresponding shear strains were computed as

$$\epsilon_{12} = \frac{1}{2} \left[\left(1 + 2 \epsilon_{11} \right) \left(1 + 2 \epsilon_{22} \right) \right]^{\frac{1}{2}} \sin \alpha_{12} \tag{15}$$

where the change of the angle between two originally orthogonal coordinate axes is given as α_{12} . It was then assumed that a linear relationship exists between the stresses (based upon undeformed dimensions) and the Lagrangian strain components. This assumption is justified only in that it leads to a successful



Comparison of Dry and Swollen Anisotropic Specimens:
a) 30-degree Unidirectional Material, and
b) An Angle-Ply Laminate Figure 2.

correlation between the analytical and experimental results for the specific materials and problem considered here. The choice of a strain tensor depends upon the magnitude of the experimental effects and is incidental to the theme of this presentation.

In the plane of a thin sheet, Equation 9 reduces to

$$\epsilon'_{11} = m^2 \epsilon_{11} + n^2 \epsilon_{22}$$

$$\epsilon'_{22} = n^2 \epsilon_{11} + m^2 \epsilon_{22}$$

$$\epsilon'_{12} = mn (\epsilon_{22} - \epsilon_{11})$$
(16)

where the x_1 axis is parallel to the fibers and x_1 is parallel to the long edge of the sheet, $m = \cos\theta$ and $n = \sin\theta$. To illustrate the transformation of Equations 16, the expansional strains ϵ_{ij}^* were measured and computed in accordance with Equations 14 and 15 as a function of θ , the data for ϵ_{11}^* being indicated in Figure 3. The solid curve signified by the term unidirectional represents the first transformation equation of (16) with $\epsilon_{11} = 0.02$ and $\epsilon_{22} = 0.75$. The shear component ϵ_{12}^* is presented in Figure 4 and is in accord with the above cited transformation rules.

To attempt the prediction of the composite expansional strains based upon its constituent material parameters, the expansional strains of the fiber and matrix, ϵ_f and ϵ_m respectively, in benzene were determined by experiments as

These values as well as the moduli presented earlier were used to compute the composite expansional strains ϵ_{11} and ϵ_{22} from Schapery's formulas which were developed for linear thermal expansion coefficients. For the longitudinal expansional strain we have

$$\epsilon_{ii} = \frac{E_{m} \epsilon_{m} v_{m} + E_{f} \epsilon_{f} v_{f}}{E_{m} v_{m} + E_{f} v_{f}}$$
(17)

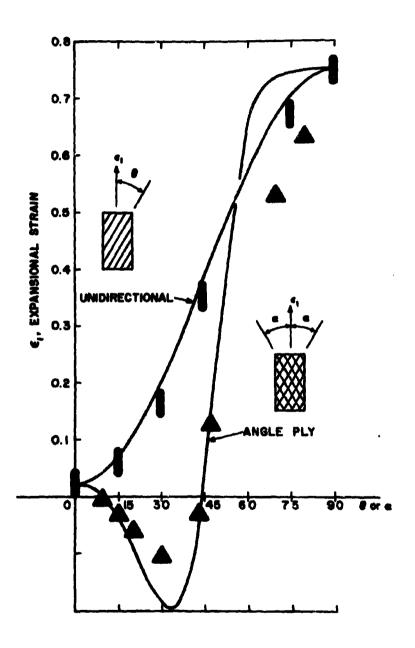


Figure 3. Comparison Between Theory and Experiment for the Expansional Strains of a Unidirectional Material and an Angle-Ply Laminate

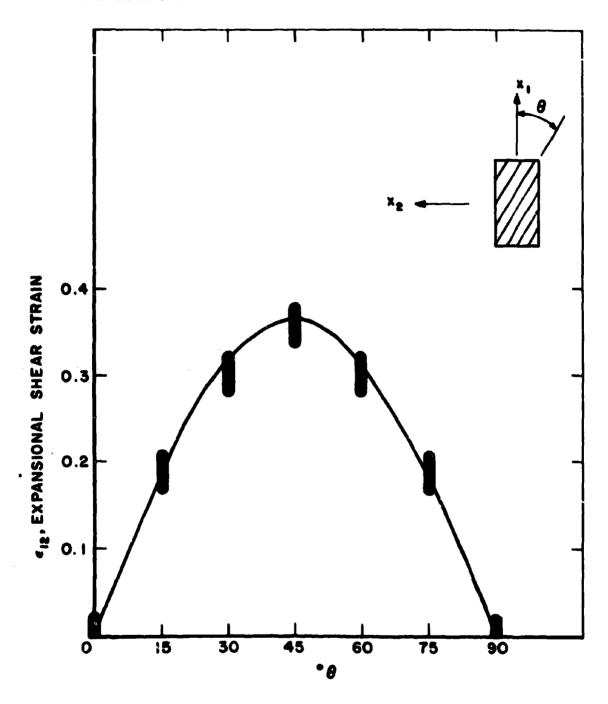


Figure 4. Comparison of Theoretical and Experimentally Observed Expansional Shear Strains for a Unidirectional Material

where v stands for volume fraction. For a volume fraction of fibers equal to 0.45 the use of Equation 17 gives

The expansional strain normal to the fiber direction is given as

$$\epsilon_{22} = (1 + \nu_m) \epsilon_m \nu_m + (1 + \nu_f) \epsilon_f v_f - \epsilon_{11} (\nu_f v_f + \nu_m v_m)$$
 (18)

which, in our composite, yields a value of 0.70. Both of these estimates are well within the limits of our experimental precision. The swelling expansion for this matrix material, $\epsilon_{\rm m}$, is in turn predictable from the well known Flory-Huggins equation in the polymer physical chemistry literature (References 3, 5, and 6). Thus we are able to form a continuous development for the calculation of a physical property ranging from the physical chemistry of constituent materials to the mechanical response of a composite material. In the next section we shall extend the theoretical chain by predicting the expansional properties of a laminate from the knowledge of the properties of the individual layers.

I AMINATE ANALYSIS

Once the expansional properties of a single layer of fiber reinforced material have been computed from the constituent material properties as discussed in the previous section, the response of a laminate (a system of unidirectional layers of various orientations) can be determined through the use of classical laminated plate theory (Reference 15). In this theory, each layer is treated as a homogeneous anisotropic material in a state of plane stress. Hence the constitutive equations for an individual layer are of the form

$$\sigma_i = Q_{ii} (e_i - e_i), i, i = 1, 2, 6$$
 (19)

where standard contracted notation (Reference 15) is now being employed, i.e., Q_{ij} representing the reduced stiffness matrix for plane stress, e_j the engineering strain components, and ϵ_j the expansional strains. In Equation 19 the normal components of stress and strain are represented by the subscripts 1 and 2, while the shear components are indicated by the subscript 6. The stress resultants N_i are then given by

$$N_{i} = \int_{-h/g}^{h/g} Q_{ij} \left(e_{j} - \epsilon_{j} \right) dz \qquad (20)$$

where h is the plate thickness. For laminates in which no bending effects are present, the strains e_i are constants; hence when $N_i = 0$, we get

$$A_{ij} = \int_{-h/2}^{h/2} Q_{ij} = \int_{-h/2}^{h/2} Q_{ij} = 0$$
 (21)

where

$$A_{ij} = \int_{-h_{A}}^{h/z} Q_{ij} dz$$
 (22)

Equation 21 defines the laminate strains under pure swelling or thermal environments, and therefore the equivalent laminate expansional strains ϵ_1 , ϵ_2 , and ϵ_6 . In what follows, we shall restrict our attention to uncoupled laminates consisting of layers of the same material and for which $A_{16} = A_{26} = 0$, so that ϵ_6 also vanishes. An example of such a laminate is a plate composed

of a series on angle-ply systems stacked symmetrically with respect to the central plane. Using the invariant properties of the reduced stiffness transformation equations (Reference 15), the expansional strains can be conviently expressed as

$$\epsilon_{1} = \frac{A_{22} R_{1} - A_{12} R_{2}}{A_{11} A_{22} - A_{12}^{2}}$$

$$\epsilon_{2} = \frac{A_{11} R_{2} - A_{12} R_{1}}{A_{11} A_{22} - A_{12}^{2}}$$
(23)

where

$$R_{1} = J_{1} h + J_{2} H_{1}$$

$$R_{2} = J_{1} h - J_{2} H_{1}$$

$$A_{11} = U_{1} h + U_{2} H_{1} + U_{3} H_{2}$$

$$A_{22} = U_{1} h - U_{2} H_{1} + U_{3} H_{2}$$

$$A_{12} = U_{4} h - U_{3} H_{2}$$

$$J_{1} = (U_{1} + U_{4}) W_{1} + 2U_{2} W_{2}$$

$$J_{2} = U_{2} W_{1} + 2W_{2} (U_{1} + 2U_{3} - U_{4})$$

$$W_{1} = \frac{1}{2} (e_{1}^{L} + e_{2}^{L})$$

$$W_{2} = \frac{1}{4} (e_{1}^{L} - e_{2}^{L})$$

$$H_{1} = \sum_{n=1}^{N} h_{n} \cos 2\theta_{n}$$

$$H_{2} = \sum_{n=1}^{N} h_{n} \cos 4\theta_{n}$$

and \leq_1^L and \leq_2^L are the layer expansional strains parallel and normal to the fibers, respectively, h is the laminate thickness, N the number of layers, θ_n the angle between the x_1 axis and the fibers in the n layer, and h_n the thickness of the n layer. The various U_i are functions of the orthotropic elastic moduli of the layers and are defined in Reference 15.

Previously reported material properties were used to compute the laminate expansional strains for angle ply composites and are shown as the "angle ply" curve in Figure 3. These calculations may be somewhat surprising in that they suggest that at certain angles, the laminate will contract in the longitudinal direction when heated or swollen Figure 2. The triangular data points were obtained from equilibrium swelling of various angle-ply samples. As indicated in the figure we have observed a 10% decrease in length for a ±15-degree laminate. Note that the 15-degree unidirectional material gave a corresponding positive expansion of 15%. Dow and Rosen (Reference 16) are observing this same effect in thermal expansion problems. The obvious agreement between theory and experiment lends confidence in the approach outlined here. Calculations of this type will have technological significance as they specify the material parameters and geometric construction necessary to yield structural elements with zero or minimal expansional coefficients.

ISOTROPIC EXPANSIONAL STRAIN IN A LAMINATE

Consider the problem of defining a lamination sequence such that the inplane expansional strain field is isotropic, i.e., the expansional normal strain is the same in every direction in the plane of the sheet, while the shear strain vanishes. A necessary and sufficient condition for this situation is that $\epsilon_1 = \epsilon_2$. In Equation 23 this occurs when the following relation is satisfied

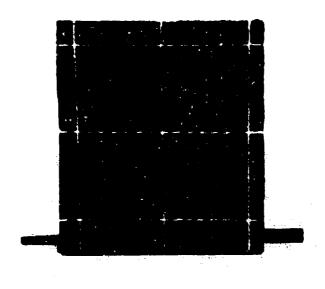
$$\frac{R_1}{R_2} = \frac{A_{11} + A_{12}}{A_{22} + A_{12}} \tag{25}$$

In general, the isotropic strain induced when Equation 26 is invoked is a function of the details of the lamination sequence. However, if we consider the case where $A_{11} = A_{22}$, we find from Equations 24 and 25 that F = 0, which implies that $R_1 = R_2 = J_1h$. If this is true we can use Equations — and 24 to obtain the following expression for the isotropic strain

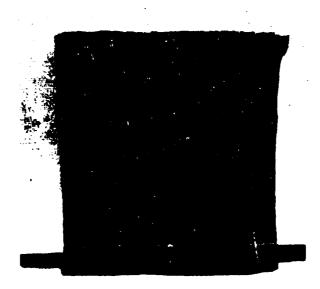
$$\epsilon = \epsilon_1 = \epsilon_2 = \frac{J_1}{U_1 + U_4} \tag{26}$$

which is an <u>invariant</u> quantity. The expression in Equation 26 depends solely on the mechanical and expansional properties of a unidirectional sheet of the laminate material. We can therefore assert the following general principle: For any uncoupled laminate with equal stiffnesses in two in-plane directions ($A_{11} = A_{22}$), the expansional strain field is isotropic in this plane and the normal strain in all directions is simply given by Equation 26. This general statement is based on the premise that all layers consist of the same material.

The statement holds despite the fact that the laminate is <u>not</u> quasi-isotropic with respect to in-plane stiffness. Examples of laminates which undergo isotropic expansional strain are 0 - 90-degree bidirectional composites, ± 45 -degree angle ply, and the combined angle ply+ α , $-\alpha$, $(\pi/2 + \alpha)$, $(\pi/2 - \alpha)$ for any value of α , all of which consist of layers of equal thickness. For a given composite material, all of these systems undergo identical expansional strains. The particular case of a 20, -20, 70, 110-degree laminate was investigated experimentally (Figure 5). In this experiment an isotropic expansional strain of 0.034 was observed; the prediction was $\epsilon_1 = \epsilon_2 = 0.027$.



(a)



(b)

Figure 5. Comparison of a) Dry and b) Swollen Composite Materials: 20, -20, 70, and-110 Degree Laminates

Equation 26 may also be expressed in terms of engineering constants as

$$\epsilon = W_1 + \frac{2 \left(E_{11} - E_{22} \right) W_2}{E_{11} + \left(1 + 2 \nu_{12} \right) E_{22}}$$
 (27)

where all moduli refer to the properties of the unidirectional material and W_1 , W_2 are given in Equations24. According to Equation 27, the isotropic strain becomes

$$\epsilon = W_1 + 2W_2 = \epsilon_1^L$$
, as $\frac{E_{11}}{E_{22}} - \infty$ (28)

Thus, for very highly anisotropic composites i.e., high ratio of E_{11}/E_{22}), the isotropic strain approaches the expansional strain of a unidirectional ply parallel to the filaments. This same limiting case may be approached by employing ribbon shaped reinforcements (Reference 19) possessing high aspect ratios. Accordingly, the material fabricator has several means at his disposal for creating a dimensionally stable material for technological applications.

Under pure thermal or swelling environments, the boundaries of a laminate are stress-free; however, each layer is subjected to stresses which can become quite large. In fact, in our swelling experiments, the induced stresses in the laminates were frequently large enough to cause delamination and fracture of the material. These internal-ply stresses can be estimated from the equations of classical laminated plate theory,

$$\sigma_i^{(n)} = Q_{ij}^{(n)} (\epsilon_i - \epsilon_j^{(n)}) \text{ for } i, j = 1, 2, 6$$
 (29)

where

$$\epsilon_{1}^{(n)} = W_{1} + 2W_{2} \cos 2\theta_{n}$$
 $\epsilon_{2}^{(n)} = W_{1} - 2W_{2} \cos 2\theta_{n}$
 $\epsilon_{4}^{(n)} = -4W_{2} \sin 2\theta_{n}$
(30)

Angle-ply thermal expansion coefficients for various composite materials are shown in Figure 6.

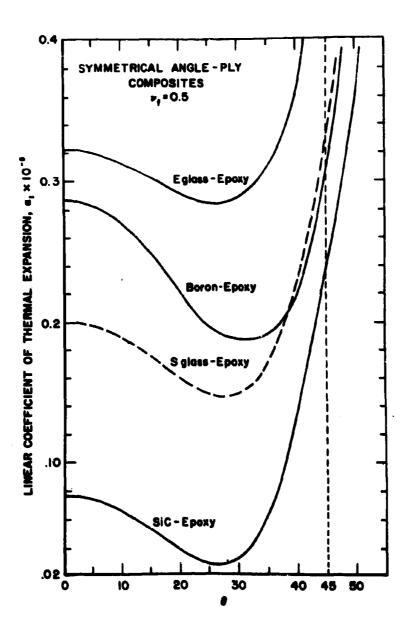


Figure 6. Comparison of Theoretical Linear Thermal Expansion Coefficients for Several Structural Composites

CONCLUSIONS

We have shown here that the changes in size and shape induced by the swelling of a solid produces effects equivalent to those caused by temperature changes. The generalized Duhamel-Neumann form of Hooke's Law can be employed to treat a wide variety of environmental problems by the joint application of solid mechanics and elementary physical chemistry. While we have limited ourselves to equilibrium problems, these results may be extended to time dependent phenomena through the structure of linear viscoelasticity (References 17 and 18) and the proper definition (Reference 17) of a new reduced time parameter $a_{\rm C}$ to account for the effects of the swelling agent on the time scale. The reduced time, ζ , for combined thermal expansion and swelling will be defined as

$$\zeta = \int_{0}^{t} \frac{d\tau}{a_{T} \left[T(x,\tau)\right] a_{C} \left[C(x,\tau)\right]}$$
(31)

as discussed in Reference 17.

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